Energy Dependence of Multielectron Transitions in X-Ray Absorption of Atoms (Commemoration Issue Dedicated to Professor Tohru Takenaka On the Occasion of His Retirement)

AUTHOR(S):

Mukoyama, Takeshi; Ito, Yoshiaki; Takahashi, Masao; Emura, Shuichi

CITATION:

Mukoyama, Takeshi ...[et al]. Energy Dependence of Multielectron Transitions in X-Ray Absorption of Atoms (Commemoration Issue Dedicated to Professor Tohru Takenaka On the Occasion of His Retirement). Bulletin of the Institute for Chemical Research, Kyoto University 1993, 71(2): 94-103

ISSUE DATE:

1993-09-30

URL:

http://hdl.handle.net/2433/77515

Bull. Inst. Chem. Res., Kyoto Univ., Vol.71, No.2, 1993

Energy Dependence of Multielectron Transitions in X-Ray Absorption of Atoms

Takeshi MUKOYAMA★, Yoshiaki ITO†, Masao TAKAHASHI* and Shuichi EMURA‡

Received June 14, 1993

The electron shakeup and shakeoff probabilities of Kr accompanying K-shell photoinonization have been calculated as a function of incident photon energy using screened relativistic hydrogenic wave functions. The calculated results show that the shakeup probability increases sharply with energy and approaches to the asymptotic value in the sudden limit at the energy close to the threshold, while the shakeoff probability increases gradually. This difference in the energy dependence indicates that the discontinuities observed in x-ray absorption spectra are mainly ascribed to the shakeup process.

KEY WORDS: Shakeup and shakeoff probabilities / Photoionization / Energy dependence

1. INTRODUCTION

The multielectron transition process in photoabsorption has been studied with great interest from early days of x-ray and electron spectroscopy. This process can be observed as satellite peaks or satellite continuum in photoelectron and Auger-electron spectra, satellite or hypersatellite peaks in x-ray emission spectra, and discontinuities in x-ray absorption spectra.

In the so-called *soft collisions* such as photoabsorption, the additional electron transition is considered to take place by the *shake* process accompanying photoionization, i.e. the rearrangement of the electron *cortège* due to inner-shell vacancy production. When a vacancy is created in an inner shell by photoionization, electrons in the same atom experience a sudden change in the central potential and have a small probability to be excited to an unoccupied state (*shakeup*) or ionized to the continuum (*shakeoff*).

With recent advent of synchrotron radiation facilities, intense monochromatic photon beams can be easily obtained and the multielectron transition in x-ray absorption has received a special attention because of its significant contributions to the near-edge structure in absorption spectra.[1] The extensive experimental studies have been reported for solids,[2-9] gases,[5,9-20] and vapors.[21]

In the case of solid targets, it was pointed out by Kodre *et al.*,[4,5,8] Frahm *et al.*,[6] and Mukoyama and Ito[9] that the oscillations of x-ray absorption spectra due to the x-ray-absorption near-edge structure (XANES) and x-ray-absorption fine structure (XAFS) would

★ 向山 毅:Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
† 伊藤嘉昭:Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
* 高橋昌男: The Institute of Scientific and Industrial Research, Osaka University, Osaka 567, Japan
‡ 江村修一: The Institute of Scientific and Industrial Research, Osaka University, Osaka 567, Japan

mask small signals of the multielectoron transition process. Recently, Li *et al.*[7] succeeded to observe the multielectron excitation processes in L-x-ray absorption spectra of RbBr and β PbO_2 by subtracting contributions of the XAFS oscillations. On the other hand, Takahashi *et al.*[22] investigated the contributions from multielectron transitions to XAFS in solid Kr. However, it is generally accepted that detection of the multielectron transitions in x-ray absorption spectra in solids is difficult because of the presence of the XANES and XAFS. Most of successful experimental observations have been performed for rare gases, where the influence of neighbouring atoms can be neglected.

Theoretically the shakeup and shakeoff probabilities in photoionization have been calculated in the sudden approximation.[23-25] In this approach, the shake mechanism is considered as a two-step process: First the inner-shell vacancy is produced by ejection of a photoelectron and another electron in the atom is excited or ionized due to the presence of the inner-shell vacancy. The shake probablitity is obtained only from the second step and independent of the incident energy of photon. This model corresponds to the case where the energy of the incident photon is much higher than the binding energy of the second electron to be excited or ionized.

When the photon energy is low and close to the shakeup or shakeoff threshold, the sudden approximation is not valid and the shake probability should be a function of the incident photon energy. The energy dependence of the shakeoff probability was first studied experimentally by Carlson and Krause.[26] They found in the K- and L-shell photoionization of Ne that the shakeoff probability becomes constant for photon energy higher than three times the threshold energy. Sachenko and Burtsev[27] calculated the K-plus-L-shell ionization cross sections as a function of photon energy and showed that the double ionization probability reaches the asymptotic value at the energy higher than 1.3 times the threshold. Using screened relativistic hydrogenic wave functions, Mukoyama[28] studied the energy dependence of the shakeoff probability accompanying K-shell photoabsorption. His results indicate that the shakeoff probability for the K-shell electron increases more slowly with energy than that for the L-subshell electrons.

For the energy dependence of the shakeup probability, Stöhr *et al.*[29] observed for nitrogen 1*s* photoemission spectra that the intensity of the shakeup peak becomes nearly uncharged at the energy very close to the threshold. In order to interpret their experimental results, Thomas[30] proposed a simple model based on the time-dependent perturbation theory. He claimed that the shakeup probability in photoionization is close to the sudden limit even at the energy corresponding to the shakeup threshold.

By observing the Auger satellite intensities in Ar as a function of photon energy, Armen *et al.*[31] measured the energy dependence of the M-shell shakeup and shakeoff probabilities during K-shell photoionization and showed that the shakeup probability has a sharp onset at the energy close to the threshold, while the shakeoff probability increases gradually. Using their results and the relative magnitude of the shakeup and shakeoff probabilities in the sudden approximation,[25] we have recently pointed out that the discontinuities observed in x-ray absorption spectra are mainly due to the shakeup precess and the shakeoff process plays a minor role.[9,19] The similar conclusion has also been obtained by Schaphorst *et al.*[20] This fact suggests that the systematic study on the energy dependence of the shakeup and shakeoff probabilities is important to interpret the multielectron transitions in x-ray absorption

spectra.

In the present work, we calculate the shakeup and shakeoff probabilities of Kr accompanying K-shell photoionization as a function of photon energy by the use of screened relativistic hydrogenic wave functions. The use of hydrogenic wave functions has an advantage that matrix elements for shakeup and shakeoff process can be expressed analytically and the numerical computations of the transition probabilities are easy. Moreover, for inner-shell electrons we have shown[28] that the screened relativistic hydrogenic model can give good approximation to the value obtained with more realistic wave functions, such as the Hartree-Fock wave functions, in the sudden limit.

However, the screened hydrogenic model would be poor for outer shells. This is especially serious in the case of the shakeup process, where the final state is in Rydberg states. Considering this fact, we calculate the shakeup and shakeoff prpbabilities in the sudden approximation with the self-consistent-field (SCF) wave functions and normalize the screened hydrogenic values for high-energy photons to the SCF values. This procedure can be justified because the behavior of the shake probability as a function of photon energy is mostly determined from the phase space sharing in the final state and the difference in wave functions has a minor effect.

2. THEORETICAL MODEL

In the present work, the shake probability is calculated under the following assumpons. First, we neglect the effect of antisymmetrization between two electrons, i.e. the photoelectron and the shake electron. In photoelectron spectra, the shakeup and shakeoff processes appear as satellite peaks or satellite continuum located near to the main peak without shake effect. This fact suggests that the shake electron have very low energy and can be distinguished from photoelectrons. In this case, the effect of antisymmetrization is small.

Second, the K-shell shake process in outer-shell photoionization is not considered. This process have the same final state as the outer-shell shake process in K-shell photoionization and cannot be separated experimentally with each other. However, it is well known in the sudden approximation[24,25] that the influence of the presence of the outer-shell vacancy on the state of the K-shell electron is very small. It is reasonable to neglect the contributions from the outer-shell vacancy.

Finally, we do not take into consideration the Coulomb interaction between the photoelectron and atomic electrons in the final state. The Coulomb collisions between two electrons can lead to additional excitation or ionization process. This process called the direct collision. We ignore this mechanism because it is considered to be small when the energy difference between two electrons is large.

According to Sauter,[32] the K-hell photoionization cross section of the atom with the atomic number Z for the incident photon energy k is given by

$$\sigma_K(W_0) = \frac{32Z^5\alpha^4}{2k^5}\phi_0(\gamma^2-1)^{3/2}\left\{\frac{4}{3}+\frac{\gamma(\gamma-2)}{\gamma+1}\left[1-\frac{1}{2\gamma(\gamma^2-1)^{1/2}}\ln\frac{\gamma+(\gamma^2-1)^{1/2}}{\gamma-(\gamma^2-1)^{1/2}}\right]\right\}, \quad (1)$$

where $\gamma = (1-\beta^2)^{1/2}$, $\beta = p/W_0$, $\phi_0 = 8/3\pi\ \alpha^3$, and p and W_0 are the momentum and the total energy of the ejected photoelectron. Throughout the present work, relativistic units ($\hbar = m = c = 1$) are used. Denoting the K-shell binding energy as B_K, the energy relation in the orinary K-shell photoionization is written as

$$W_0 = k + 1 - B_K . \tag{2}$$

In the shakeup process where an i-shell electron makes a transition to a j shell in the final state during K-shell photoionization, the cross section can be given by

$$\sigma^{su} = n_i \left| \langle \psi'_j \mid \psi_i \rangle \right|^2 \sigma_K (W_1) , \tag{3}$$

where n_i is number of $_i$-shell electrons, ψ_i is the i-shell electron wave functon in the ground-state atom and ψ'_j is the j-shell electron wave function in the atom with a K-shell vacancy. The energy relation is given as

$$W_1 = k + 1 - B_K - B_i + B'_j, \tag{4}$$

where B_i and B'_j are the binding energy of the i-shell electron in the initial state and that of the j-shell erectron in the atom with K-shell vacancy.

The shakeoff probability in K-shell photoionization is written in the same manner as in the previous work[28]

$$\sigma^{so}(W_2)\, dW_2 = \frac{n_i}{2\pi^2} \left| \langle \psi'_f \mid \psi_i \rangle \right|^2 \sigma_K (W_1)\, p_2 W_2 dW_2, \tag{5}$$

where ψ'_f is the continuum wave function of the electron in the atomic field with K-shell vacancy, p_2 and W_2 are the momentum and the total energy of the shakeoff electron, and $\sigma_K (W_1)$ is the K-shell photoionization cross section for the incident photon with energy k and for the total energy of the photoelectron W_1. The energy relation corresponding to Eq. (5) is

$$W_1 + W_2 = k + 2 - B_K - B_i . \tag{6}$$

Here B_i is the binding energy of the shakeoff electron before ejection.

From Eqs. (1), (3), and (5), the shakeup and the shakeoff probability as a function of the photon energy k is obtained as

$$P^{su}(k) = \sigma^{su} / \sigma_K (W_0) , \tag{7}$$

and

$$P^{so}(k) = \int_1^{W_{max}} dW_2 \sigma^{so}(W_2) / \sigma_K (W_0), \tag{8}$$

where W_{max} is the maximum energy available for the shakeoff electron and expressed as

$$W_{max} = k + 1 - B_K - B_i. \tag{9}$$

The atomic matrix elements in Eqs. (3) and (5) are calculated analytically using the relativistic hydrogenic wave functions.[33] The relevant expressions for the shakeoff process were already derived by us and given as Eqs. (5), (6) and (9) in our paper.[34] The matrix element for the shakeup process is also obtained in the similar manner:

$$M_A = C\,[L_+ + L_-]\ , \tag{10}$$

$$C = N_1 N_2\ (2\lambda_1)^{\gamma_1 - 1}\ (2\lambda_2)^{\gamma_2 - 1},$$

$$L_\pm = [(1 \pm W_1)\ (1 \pm W_2)]^{1/2}\ \{n_1' n_2 J_{11} \pm n_1'\ (\kappa - \zeta_2/\lambda_2)\ J_{10} \pm n_2\ (\kappa - \zeta_1/\lambda_1)\ J_{01} + (\kappa - \zeta_1/\lambda_1)\ (\kappa - \zeta_2/\lambda_2)\ J_{00}\}\ ,$$

$$J_{ij} = \frac{\Gamma(\gamma_1+\gamma_2+1)}{(\lambda_1+\lambda_2)^{\gamma_1+\gamma_2+1}} \sum_{m=0}^{\infty} \frac{(n_1'+i)_m (\gamma_1+\gamma_2+1)_m}{(2\gamma_1+1)_m\, m!}$$

$$\times \left(\frac{2\lambda_1}{\lambda_1+\lambda_2}\right)^m\ {}_2F_1\left(-n_2' + j, \gamma_1 + \gamma_2 + 1 + m; 2\gamma_2 + 1; \frac{2\lambda_2}{\lambda_1+\lambda_2}\right),$$

$$N_i = -\frac{2^{1/2}\lambda_i^{5/2}}{\Gamma(2\gamma_i+1)} \left[\frac{\gamma(2\gamma_i+n_i'+1)}{n_i'!\zeta_i(\zeta_i-\lambda_i\kappa)}\right]^{1/2}, \tag{10'}$$

$$W_i = \left[1 + \left(\frac{\zeta_i}{n_i'+\zeta_i}\right)^2\right]^{-1/2},$$

where $(j)_m = j(j+1)\ldots(j+m-1) = \Gamma(j+m)/\Gamma(j)$, $\lambda_i = (1 - W_i^2)^{1/2}$, $\zeta_i = \alpha Z_i$ and $\gamma_i = (\kappa_i^2 - \zeta_i^2)^{1/2}$.

In order to take into accout the effect of Coulomb interaction between electrons, the screening-correction method is used and the atomic number Z in the hydrogenic wave functions is replaced by an effective nuclear charge $Z_{eff} = Z - \sigma$, where σ is the screening constant.

For the initial state, the screening constant is determined from the relation[35]

$$\sigma = Z\ (1 - \vec{r}_Z/\vec{r}_{SCF})\ , \tag{11}$$

where $\vec{r}_Z$ is the mean radial distance of the electron in the initial state for the relativistic hydrogenic wave function and $\vec{r}_{SCF}$ is that calculated with the self-consistent-field (SCF) wave function. The general expression for $\vec{r}_Z$ for an arbitrary shell is given Eq. (11) in Ref.34. The numerical value for $\vec{r}_{SFC}$ is calculated by the use of the Dirac-Fock-Slater (DFS) program similar to that of Liberman *et al.*[36]

In our previous works on the shakeoff process,[28,34] we estimated the screening constant for the final continuum state as follows. First we assume that the screening constant for the continuum electron is same as that for the bound state before ejection. Then the value is modified to take into consideration the presence of the inner-shell vacancy by multiplying the ratio of the Slater's screening constants[37] with and without the vacancy.

In the present work, we calculated the screening constants using Eq. (11) for the final excited states in the shakeup process and for the continuum states in the shakeoff process. In order to use Eq. (11) in the final state, we performed the DFS calculations for the atom with a K-shell vacancy and obtained the SCF field in the final-state atom. The Dirac equation with this atomic potential is solved for each electronic state and its mean radial distance is calculated. Using the $\vec{r}_{SCF}$ value thus obtained, the screenig constant is determined from Eq. (11) . The screening constant for the continuum state is taken to be same as that for the bound state before ejection in the final state.

3. RESULTS AND DISCUSSION

Calculations for the shakeup and shakeoff probabilities accompanying K-shell photoionization have been performed as a function of photon energy for all L, M, and N subshells in Kr by the use of screened hydrogenic model. In order to normalize these probabilities at high energy, the shakeup and shakeoff probabilities in the sudden approximation are calculated relativistically with the DFS wave functions.[38] The wave functions and the atomic potentials are obtained both for the initial state, a neutral Kr atom, and for the final state, a positive ion with K-shell vacancy, in the DFS model.[36] The shakeup and shakeoff probabilities are calculated in the manner similar to the nonrelativistic case in our previous work.[25]

First, the calculation of the shakeup-plus-shakeoff probability for a certain subshell is made with the method of Carlson and Nestor.[23] Then the shakeup probabilities to various Rydberg states are evaluated. The wave functions for final excited states are obtained by solving the Dirac equation in the central field for the positive ion. The total shakeup probability is estimated as a sum of these partial shakeup probabilities up to $n = 20$. The shakeoff probability is obtained by subtracting the shakeup probability from the shakeup-plus-shakeoff probability. The shakeup and shakeoff probabilities in the screened hydrogenic model are normalized to the corresponding DFS values at the photon energy of 500 keV. All the numerical computations of the presenet work have been carried out on the FACOM M-760/10 computer in Institute for Chemical Research, Kyoto University.

Figure 1 shows the energy dependence of the shake probabilities for the L_1 shell. The dashed curve indicates the shakeup probability and the dot-dashed curve represents the shakeoff probability. The sum of both probabilities is shown by the solid curve. As has been

pointed out in the nonrelativistic case,[25] the shakeoff probability is larger than the shakeup probability for inner-shell electrons. However, the probabilities are very small, $\sim 10^{-5}$.

The results for the M_1 and M_3 shells are given in Figs. 2 and 3. For these subshells, the shakeoff probability is still larger than the shakeup probability in the high-energy region. However, the probabilities are in order of 10^{-3}. It should be noted also that in the energy region close to the threshold the shakeup process has a sharp onset, while the shakeoff probability increases gradually. This situation is more clearly demonstrated in Fig. 4 for the M_5 shell and in Fig. 5 for the N_3 shell. The similar trend has already been observed by Armen *et al.*[31] for the M shell in Ar accompanying K-shell photoionization. The theoretical calculations by Schaphorst *et al.*[20] for the $3d$ and $4p$ shells in Kr also support the experimental results.

This fact indicates that the discontinuities observed in x-ray absorption spectra can be mainly ascribed to the shakeup process only, as pointed out by us[19] and by Schaphorst *et al.*[20] It is also improtant to note that in x-ray absorption spectra it is difficult to detect multielectron transitions involving inner-shell electrons in K-shell photoionization, because the contribution from the shakeup process for these electrons is small.

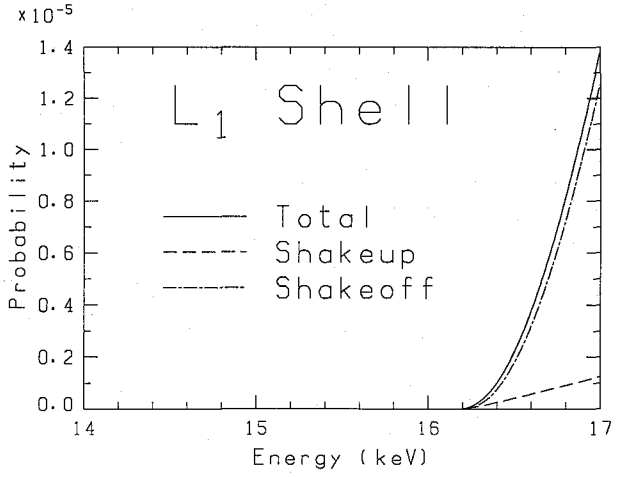

Fig. 1. Energy dependence of shakeup and shakeoff probabilities for L_1-shell electrons in Kr accompanying K-shell photoionization. The dashed curve indicates the shakeup probability, while the dot-dashed curve represents the shakeoff probability. The sum of two probabilities is shown by the solid curve.

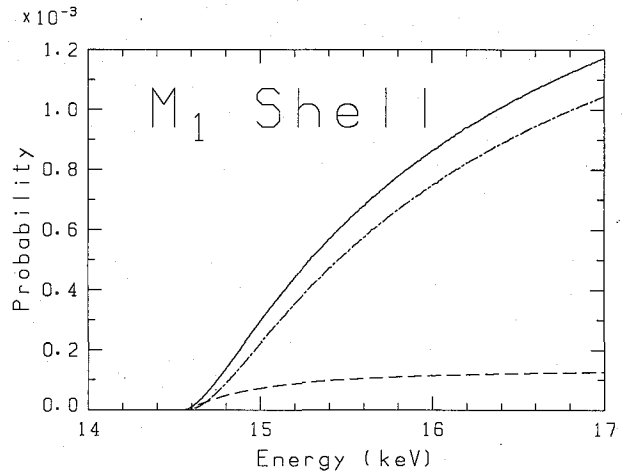

Fig. 2. Same as Fig.1, but for M_1-shell electrons.

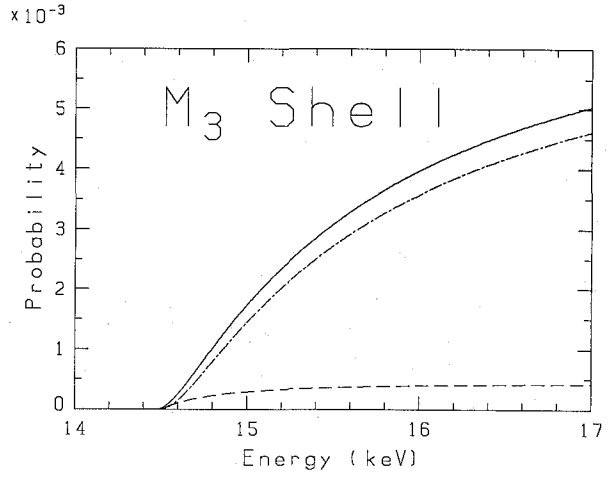

Fig. 3. Same as Fig.1, but for M_3-shell electrons.

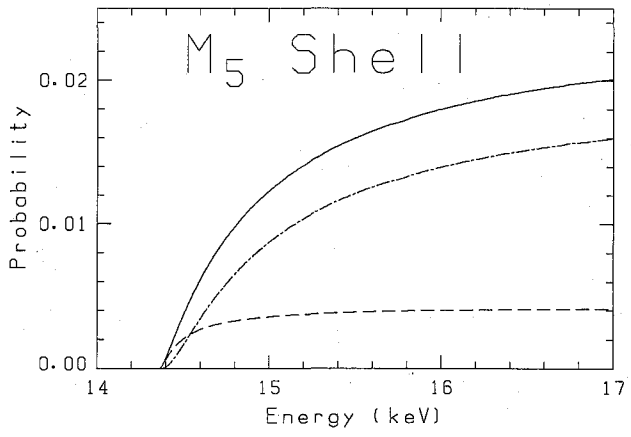

Fig. 4. Same as Fig.1, but for M_5-shell electrons.

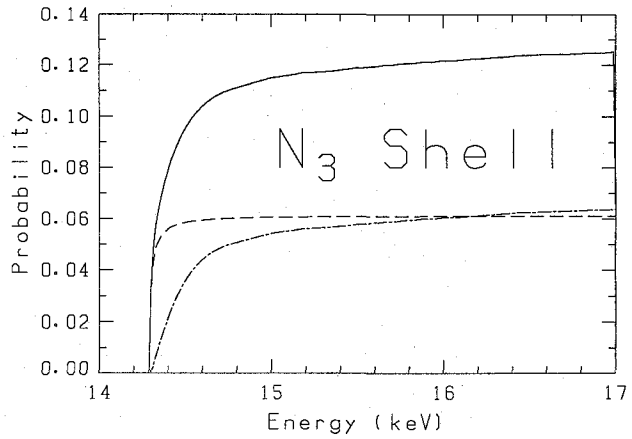

Fig. 5. Same as Fig.1, but for N_3-shell electrons.

REFERENCE

(1) B. Crasemann, in "Electronic and Atomic Collisions, Invited Papers, Proc. XVII Intern. Conf. on the Physics of Electronic and Atomic Collisions, 10-16 July, Brisbane, Australia," ed. by W.R.MacGilliovray, I.E.McGarthy, and M.C.Strange, Adams Hilger, Bristol, (1992), p. 69.
(2) M.Deutsch and M.Hart, *Phys. Rev.* A, **29**, 2946(1984).
(3) M.Deutsch, M.Hart, and P.Durham, *J. Phys.* B, **17**, L395(1984).
(4) A.Kodre, M.Hribar, I.Arcon, D.Glavic, R.Frahm, and W. Drube, HASYLAB Jahresbericht 1989, HASYLAB, Hamburg, (1989), p.215.
(5) A. Kodre, S.J.Schaphorst, and B.Crasemann, in "Proc. 15th Intern. Conf. on X-Ray and Inner-Shell Processes, July 9-13 1990, Knoxville" ed. by T.A.Carlson, M.O. Krause, and S.T.Manson, American Institute of Physics, New York, (1991), p. 582.
(6) R.Frahm, W.Drube, I.Arcon, D.Glavic-Cindro, M.Hribar, and A.Kodre, in "Proc. 2nd Conf. on Progress in X-Ray Synchrotron Radiation Research, Rome, 1989," ed. by A.Balerna, E.Bernieri, and S.Mobilio, Societa Italiana di Fizica, Bologna, (1990), p. 129.
(7) G.Li, F.Bridges, and G.S.Brown, *Phys. Rev. Lett.*, **68**, 1609(1992).
(8) A. Kodre, H.Hribar, I.Arcon, D.Glavic-Cindro, M.Stuhec, R.Frahm, and W.Drube, *Phys.* Rev. *A*, **45**, 4682(1992).
(9) T.Mukoyama and Y.Ito, in "Proc. SPring-8 Workshop: Atomic Physics at High Brilliance Radiation Facilities, March 23-24 1992, Himeji," RIKEN, Wako, Japan, (1993),p. 129.
(10) B.M.Kincade and P.Eisenberger, *Phys. Rev. Lett.*, **34**, 1361(1975).
(11) R.D.Deslattes, R.E.LaVilla, P.L.Cowan, and A.Henins, *Phys. Rev. A*, **27**, 923(1983).
(12) M.Deutsch and M.Hart, *Phys. Rev. Lett.*, **57**, 1556 (1986) ; *Phys. Rev. A*, **34**, 5168(1986).
(13) E.Bernieri and E.Burattini, *Phys. Rev. A*, **35**, 3322(1987).
(14) S.Bodeur, P.Millič, E.Lizon á Lugrin, I.Nenner, A.Filipponi, F.Boscherini, and S.Mobiloi, *Phys. Rev. A*, **39**, 5075(1989).
(15) G.Brill, M.Deutsch, P.Kizler, W.Drube, and R.Frahm, HASYLAB Jahresbericht 1989, HASYLAB, Hamburg, (1989), p. 157.
(16) M.Deutsch, G.Brill, and P.Kizler, *Phys. Rev. A*, **43**, 2591(1991).
(17) U.Kuetgens and J.Hormes, *Phys. Rev. A*, **44**, 264(1991).
(18) M.Deutsch and P.Kizler, *Phys. Rev. A*, **45**, 2119(1992).
(19) Y.Ito, H.Nakamatsu, T.Mukoyama, K.Omote, S.Yoshikado, M.Takahashi, and S.Emura, *Phys.*

Rev. A, **46**, 6083(1992).
(20) S.J.Schaphorst, A.F.Kodre, J.Ruscheinski, B.Crasemann, T.Åberg, J.Tulkki, M.H.Chen, Y.Azuma, and G.S.Brown, *Phys. Rev. A*, **47**, 1953(1993).
(21) M.H.Tuillier, D.Laporte, and J.M.Esteva, *Phys. Rev.* A, **26**, 37(1982).
(22) M.Takahashi, S.Emura, F.Kanamaru, K.Omote, S.Yoshikado, Y.Ito, and T.Mukoyama, *Bull. Inst. Chem. Res., Kyoto Univ.*, **71**, 37(1993).
(23) T.A.Carlson and C.W.Nestor, *Phys. Rev. A*, **8**, 2887(1973).
(24) T.Mukoyama and K.Taniguchi, *Phys. Rev. A*, **36**, 693(1987).
(25) T.Mukoyama and K.Taniguchi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **70**, 1(1992).
(26) T.A.Carlson and M.O.Krause, *Phys. Rev.*, **140**, A1037(1695).
(27) V.P.Sachenko and E.V.Burtsev, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **31**, 964, (1967) [*Bull. Acad. Sci. USSR, Phys. Ser.*, 31, 980(1968)].
(28) T.Mukoyama, *Bull. Inst. Chem. Res., Kyoto Univ.*, **64**, 1(1986).
(29) J.Stöhr, R.Jaeger, and J.J.Rehr, *Phys. Rev. Lett.*, **51**, 821(1983).
(30) T.D.Thomas, *Phys. Rev. Lett.*, **52**, 417, 1984.; *J. Elec. Spectrosc. Relat. Phenom.*, **40**, 259 (1986).
(31) G.B.Armen, T.Åberg, K.R.Karim, J.C.Levin, B.Crasemann, G.S.Brown, M.H.Chen, and G.E.Ice, *Phys. Rev. Lett.*, **54**, 182(1985).
(32) F.Sauter, *Ann. Physik*, **9**; 21 (1931) ; **11**, 452(1931).
(33) M.E.Rose,"Relativistic Electron Theory," Wiley, New York(1961).
(34) T.Mukoyama and S.Shimizu, *Phys. Rev. C*, **11**, 1353(1975).
(35) T.A.Carlson, C.W.Nestor, Jr., T.C.Tucker, and F.B.Malik, *Phys. Rev.*, **169**, 27(1968).
(36) D.A.Liberman, D.T.Cromer, and J.T.Waber, *Comput Phys. Commun.*, **2**, 107(1971).
(37) J.C.Slater, *Phys. Rev.*, **36**, 57(1930).
(38) T.Mukoyama and Y.Ito, to be published.